

February 17, 2004

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Re: Twenty-Sixth Monthly Report #NDJ-2-30630-11

Dear Harin,

This letter comprises the monthly technical status report for ITN's subcontract # NDJ-2-30630-11, "Plasma-Assisted Coevaporation of S and Se for Wide Band Gap Chalcopyrite Photovoltaics", under the Thin Film Partnership Program. The reported work was performed during the second month of phase 3 for this contract (twenty-sixth month overall), which is January 7, 2004 through February 7, 2004. This report describes activities performed by ITN, as well as those performed by lower-tier subcontractor Colorado School of Mines (CSM), under the direction of Dr. Colin Wolden.

## 1. Program Goals and Approach

Our primary objective under this program is to determine if the chalcogen in CIGS co-evaporation can be delivered more effectively by activation with a plasma. Possible advantages of plasma-assisted co-evaporation (PACE) are

- increased utilization of chalcogens,
- decreased deposition temperatures,
- decreased deposition times, and
- increased ability to tailor S/Se ratio.

University researchers at CSM are developing and testing the fundamental chemistry and engineering principles. Industrial researchers at ITN are adapting PACE technology to CIGSS co-evaporation and validating PACE process for fabrication of thin film PV.  $\text{In}_2\text{Se}_3$  films, which are used as precursor layers in high-efficiency CIGS depositions, were used as the first test case for the examining the advantages of PACE listed above, and significant advantages were demonstrated. Presently, the examination is being extended to the complete high-efficiency three-stage CIGS co-evaporation process.

## 2. Incorporation of PACE Sources Into Three-Stage Deposition

In last month's report, Phase III work for incorporating PACE sources into the three-stage CIGS process was outlined in terms of the schedules for five areas of activity: uniformity and rate characterization, rate control and procedures in bell jar, compatible three-stage metals flux control, source installation, and PACE CIGS fabrication. This month, work was performed on uniformity and rate characterization, compatible three-stage metals flux control, and source installation, with all activities progressing on or ahead of schedule.

### 2.a. Uniformity and Rate Characterization

An understanding of the flux profile from the PACE sources is very important to determining acceptable geometries for installation of the PACE sources in the CIGS three-stage bell jar. A thorough characterization this month of the flux profile from the PACE source indicates that flux follows the expected  $1/r^2$  fall-off with distance from the source, as well as the expected<sup>1</sup>  $\cos^3\theta$  dependence of flux per solid angle on azimuthal angle, independent of Se rate and Ar pressure.

The PACE source was operated at a variety of Se rates and Ar pressures, with witness slides placed around the source in the configuration of Figure 1. Se thickness at several points on each witness slide was measured by mechanical profilometer. In Figure 1,  $z$  is the vertical distance from the source aperture to the plane of a given witness slide.  $R$  is the distance from the aperture to any measurement point, and  $\theta$  is the angle between  $\vec{R}$  and the source axis. If flux per solid angle follows a  $\cos^n\theta$  dependence and is constant with increasing  $R$  (i.e. neither Se-Se nor Se-Ar collisions cause significant spreading of the flux after it leaves the aperture), then it can be derived that

$$\frac{\text{Flux at measurement point } (z, R)}{\text{Flux on axis at distance } z_0} = \left(\frac{z}{R}\right)^{3+n} \left(\frac{z_0}{z}\right)^2 \quad (i)$$

This expression includes the necessary factors for dependence of flux on  $\theta$ , distance to slide, and angle between slide and direction of flux. A similar expression can be derived for a source axis that is not normal to the substrate plane.

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<sup>1</sup> R.W. Birkmire, W.N. Shafarman, E. Eser, S.S. Hegedus, B.E. McCandless, R. Aparicio, K. Dobson, "Optimization of Processing and Modeling Issues for Thin Film Solar Cell Devices Including Concepts for the Development of Polycrystalline Multijunctions", *Annual Report to NREL under Subcontract ZAK-8-17619-33*, 2001, pp. 3-4.

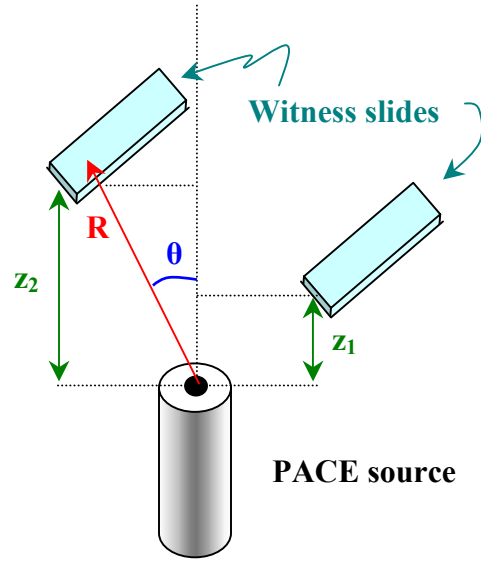


Figure 1: Configuration for measuring flux distribution of PACE source.

Experimental verification of the expected flux profile (i) for multiple source operating conditions is shown in Figure 2. In Figure 2a, discrete points show thickness measured on multiple witness slides (as per Figure 1) graphed against  $R$ . Lines show a least squares fit to the flux profile, with  $n$  as the adjustable parameter. Figure 2b lists the test conditions and best fit  $n$  for each deposition. The distribution is invariant over the range explored: 3x variations in Ar pressure, 2x variations in rate, and 2x variations in distance.

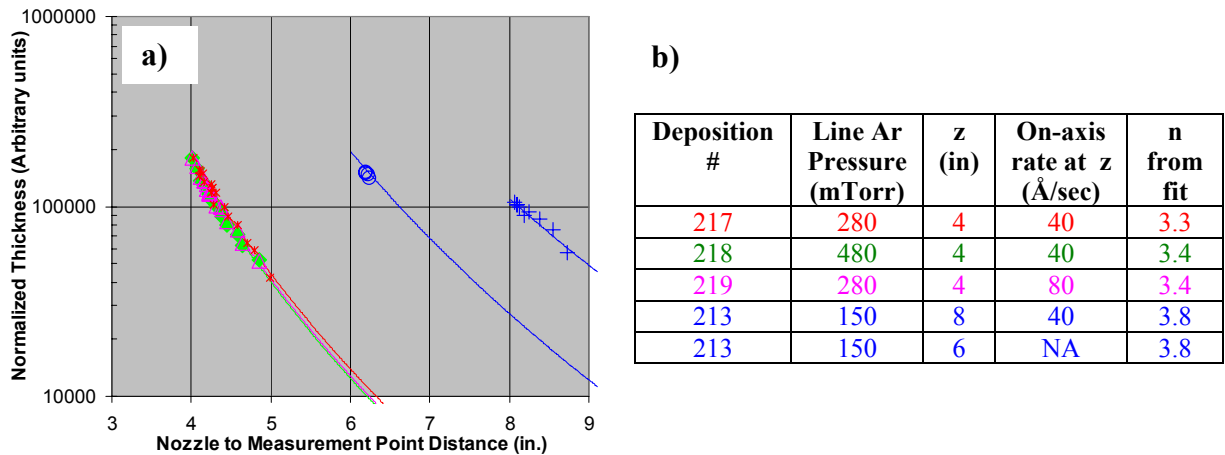


Figure 2: Measurements of PACE source flux profile under different operating conditions.

Flux to the substrate and its uniformity can now be predicted for any geometric configuration of the PACE source into the three-stage CIGS bell jar. A suitable location has been identified, and fabrication of mounting brackets is underway.

### ***2.b. Compatible Three-Stage Metals Flux Control***

In order to avoid interference between the electron impact emission spectrometer (EIES) rate monitor and Ar from the PACE sources, an alternate rate control deposition procedure was implemented. Metals source rates were set using the EIES (without Ar flowing to the PACE source), to establish a necessary source power for each desired rate and momentary boat charge and resistance. This pre-run calibration could also be performed using a quartz crystal microbalance. Then, the three-stage recipe was executed without EIES control, applying the derived sources powers to achieved the prescribed rates. The appropriate times to end the first, second, and third stages were deduced from the substrate's IR emission characteristics.<sup>2</sup> A CIGS film with the correct thickness, composition, and maximum and final Cu ratios was obtained. This film is currently being processed into devices.

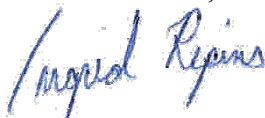
### ***2.c. Source Installation***

Progress was made this month in several aspects of the installation of the PACE sources in the three-stage CIGS bell jar. A statement of work specifying the necessary electrical modifications to bell jar was drafted for the ITN equipment build group. Several options for placement of RF, Ar, and power feedthroughs were evaluated. Measurements were taken for preliminary design of bracketing holding PACE source in chamber. A power controller for the Se pot nozzle heater was obtained and tested. At CSM, improvements to RF matching and elimination of stray capacitances were made.

## **3. Team Activities**

ITN and CSM participate in CIS team activities. This month, a draft outline with figures, for a possible publication describing the absorber sub-team's study of transport-related absorber measurements, was completed. Billy Stanbery is currently reviewing the outline, and it will be distributed for review and modification to all interested participants shortly.

Best Wishes,



Ingrid Repins  
Principal investigator  
ITN Energy Systems

Cc: Ms. Carolyn Lopez; NREL contracts and business services  
Dr. Colin Wolden; CSM technical lead

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<sup>2</sup> See "Tolerance of Three-Stage CIGS Deposition to Variations Imposed by Roll-to-Roll Processing: Phase I Annual Report", May 2002--May 2003, <http://www.nrel.gov/docs/fy03osti/34314.pdf>, for a description of stage endpoint detection by substrate IR emission.